



Femtosecond X-ray Science at the ALS

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Outline

Scientific Motivation

- structural dynamics in condensed matter on femtosecond time scale

Current and Future Research Areas

- ultrafast phase transitions (order/disorder and solid/solid)
- structural dynamics of molecular transition states
- structural dynamics of ultrafast biological processes

Generation of femtosecond x-rays at the ALS

- femtosecond slicing of electron beam
- results from proof-of-principle experiments

Femtosecond X-ray Science at the ALS



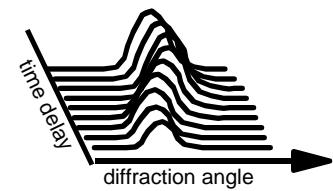
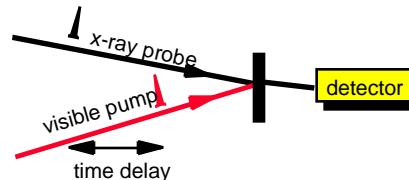
Structural Dynamics in Condensed Matter

fundamental time scale for atomic motion
vibrational period: $T_{\text{vib}} \sim 100 \text{ fs}$

- ultrafast chemical reactions
- ultrafast phase transitions
- surface dynamics
- ultrafast biological processes

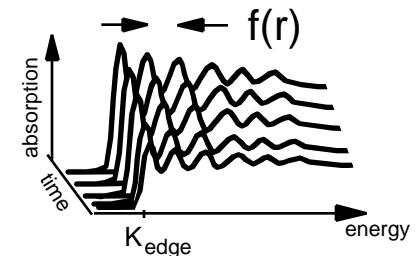
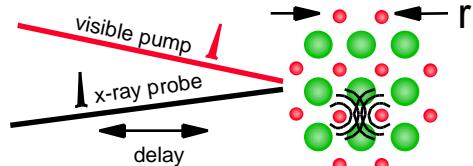
Rapidly emerging field of research
Physics, Chemistry and Biology

time-resolved x-ray diffraction



ordered crystals - phase transitions, coherent phonons

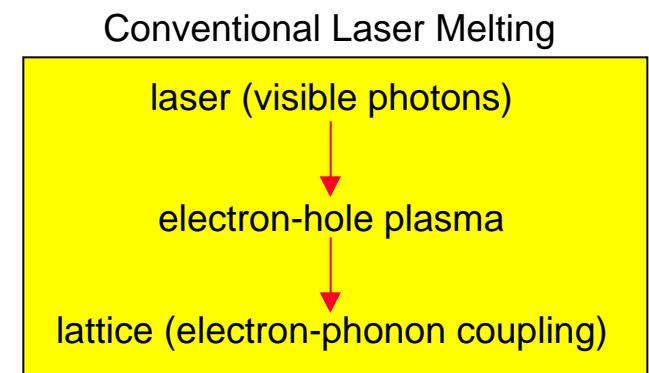
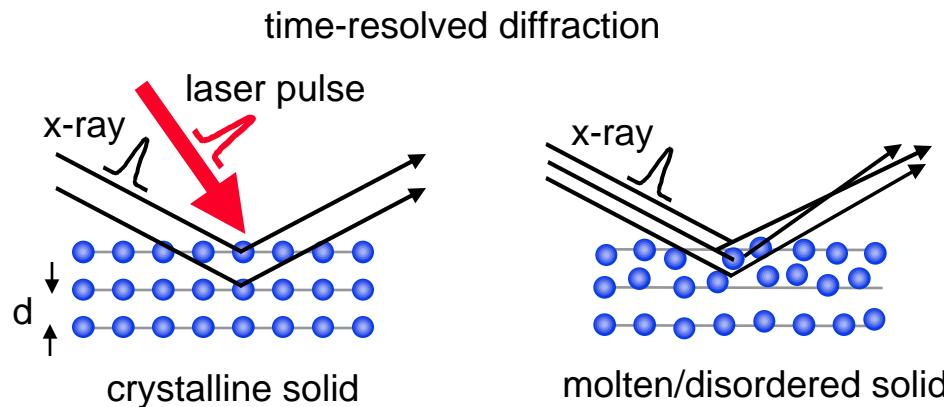
time-resolved EXAFS, NEXAFS, surface EXAFS



complex/disordered materials - chemical reactions
surface dynamics
bonding geometry

Laser-Induced Solid/Liquid Phase Transition

Can a solid/liquid phase transition occur on the time scale of a vibrational period?



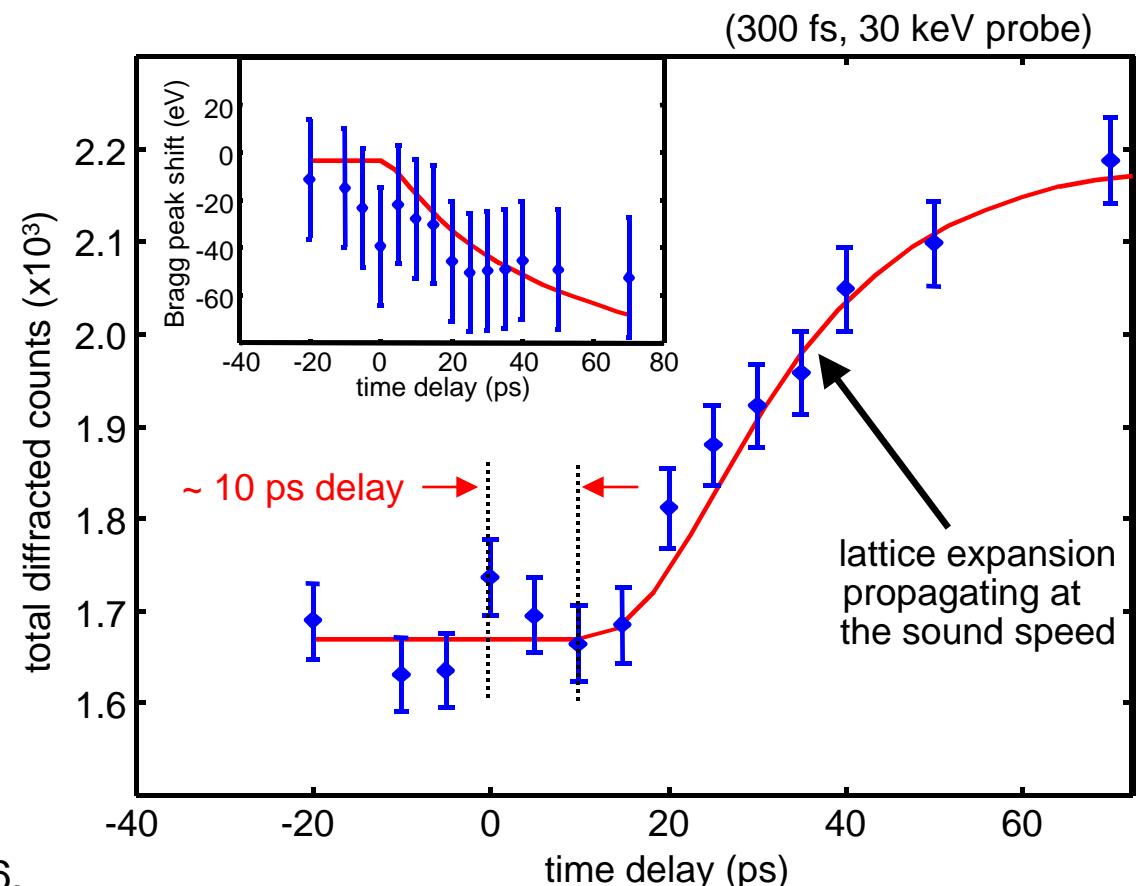
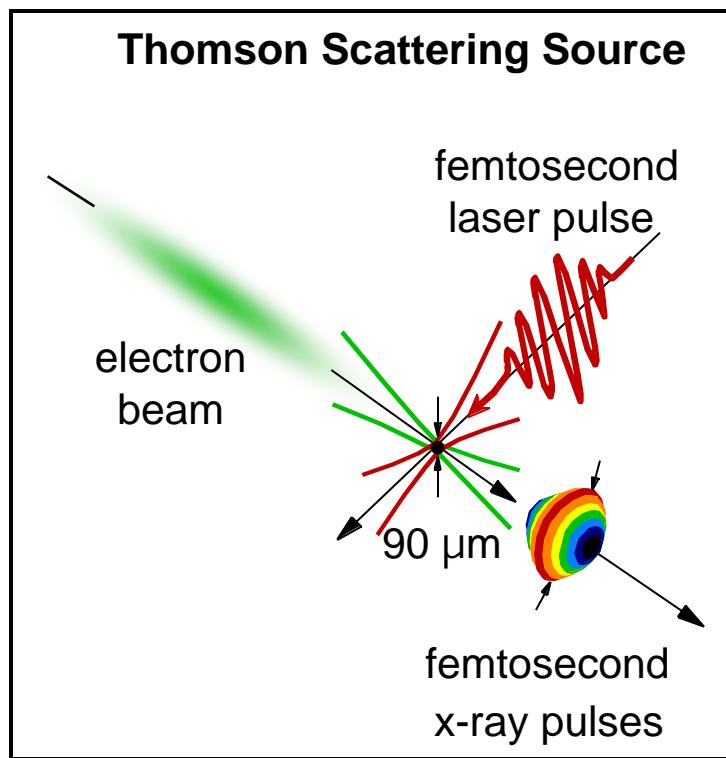
Nonequilibrium Conditions (femtosecond optical excitation)

- electron temperature \gg lattice temperature
- no equilibration of vibrational modes (vibrational coherence)

Ultrafast Phase Transition

- lattice instabilities result from high density e-h plasma
- vibrational motion $\sim 10^5$ cm/sec \longrightarrow (1 Å in 100 fs)

Laser Heated InSb Data



Leemans et al., *Phys. Rev. Lett.*, 1996.

Schoenlein et al., *Science*, 1996.

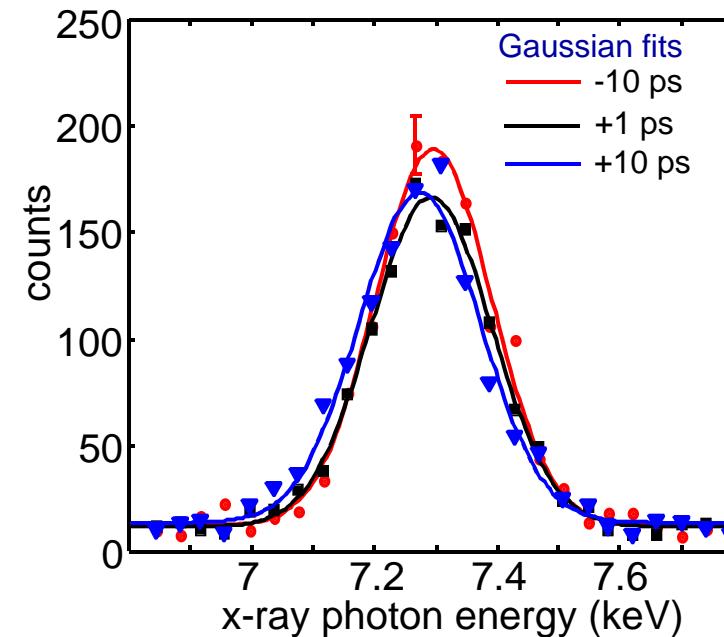
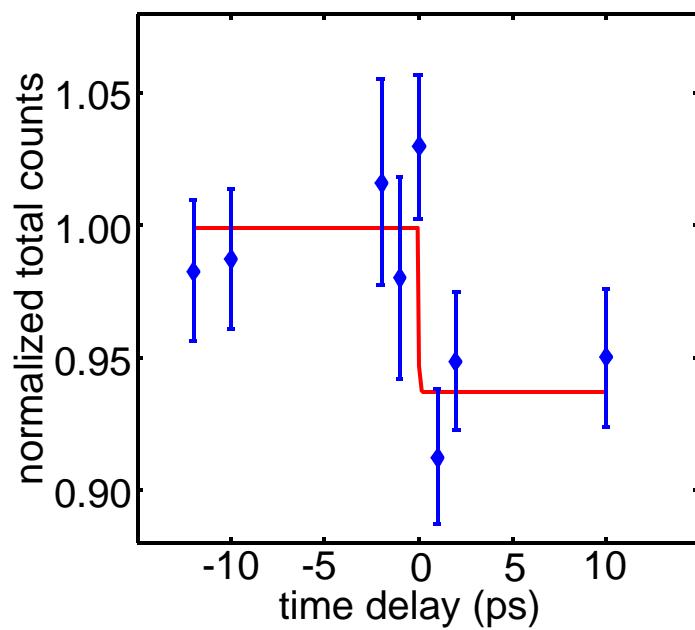
Indication of Ultrafast Disordering



- ~6 % reduction in integrated diffracted photons for $\text{delay} < 1 \text{ ps}$
- sub-picosecond formation of $\sim 30 \text{ \AA}$ melt depth
- higher sensitivity to the surface

7.5 keV photons from Thomson source (25 MeV e-beam)

InSb 12.8 degrees off (111)



Chin et al., *Phys. Rev. Lett.*, 1999.



Ultrafast Structural Dynamics in Crystalline Solids

beyond Bragg studies of order disorder transitions

Femtosecond NEXAFS and EXAFS experiments

- amorphous/polycrystalline materials
- surface sensitivity
- changes in coordination and bonding

Initial Experiments on proposed beamline 5.3.1:

- semiconductors - structural dynamics of semiconductor/metal transition
- graphite (diamond) - evolution of liquid carbon

Future experiments on nanocrystal materials

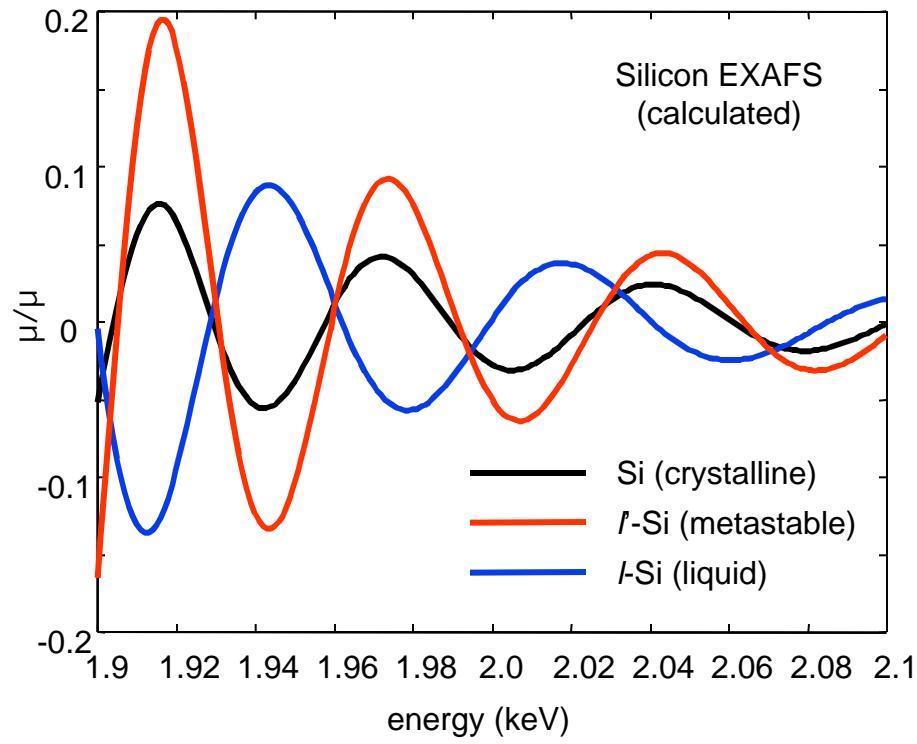
- reversible solid/solid phase transitions

Silicon - Metastable Liquid Phase

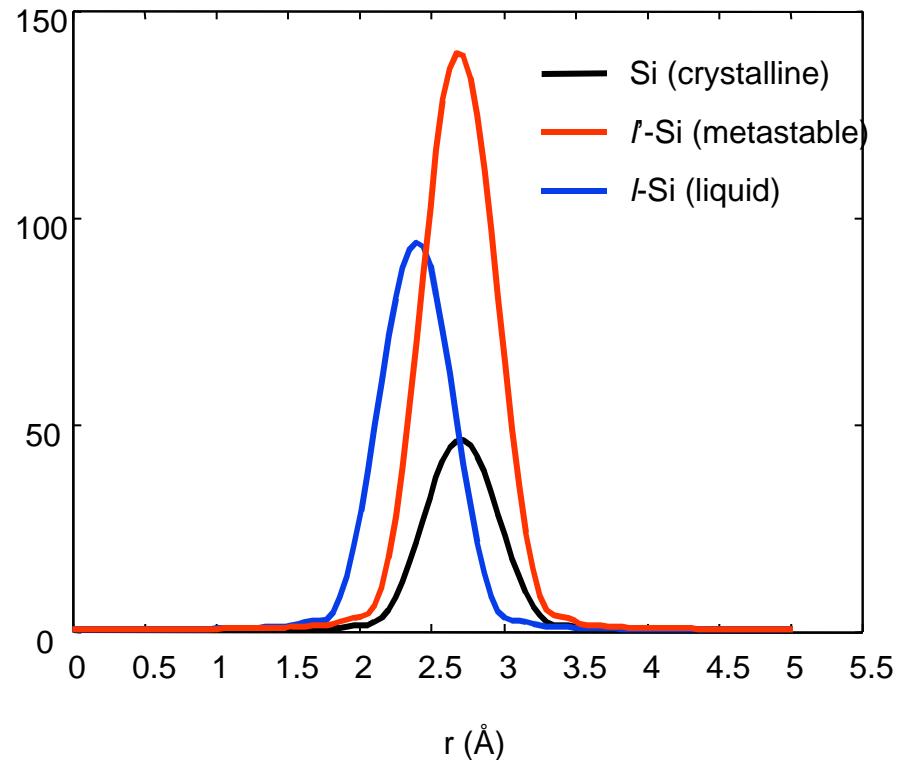


- ab initio molecular dynamics simulations
- ultrashort laser pulse heating

P.L. Silvestrelli et al



	r (Å)	coordination
Si (crystalline)	2.7	4
<i>l</i> -Si (metastable)	2.7	11-13
<i>l</i> -Si (liquid)	2.4	6-7



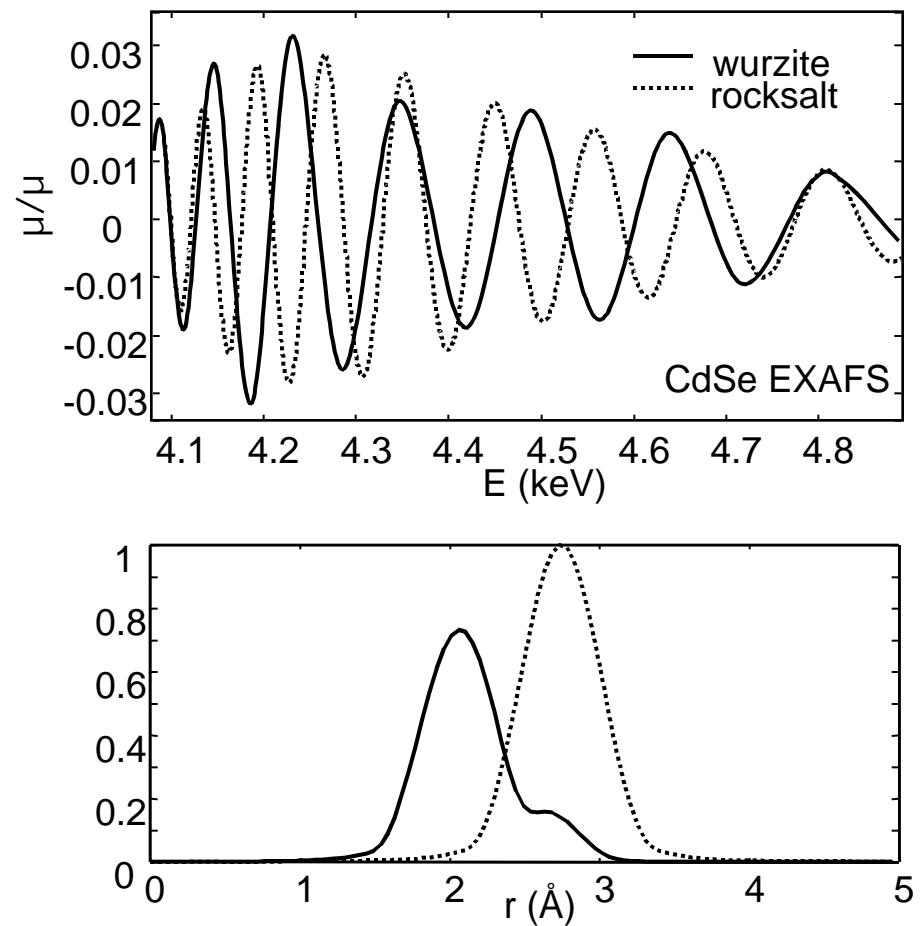
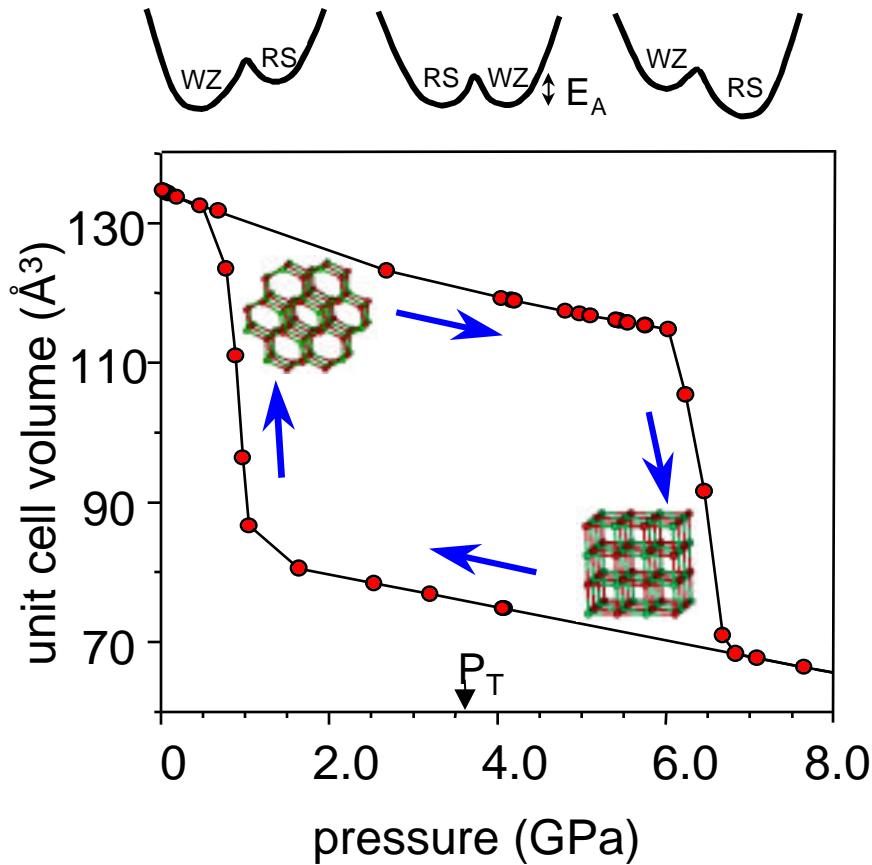
Reflectivity EXAFS: $\sim 10^7$ photons for S/N~1

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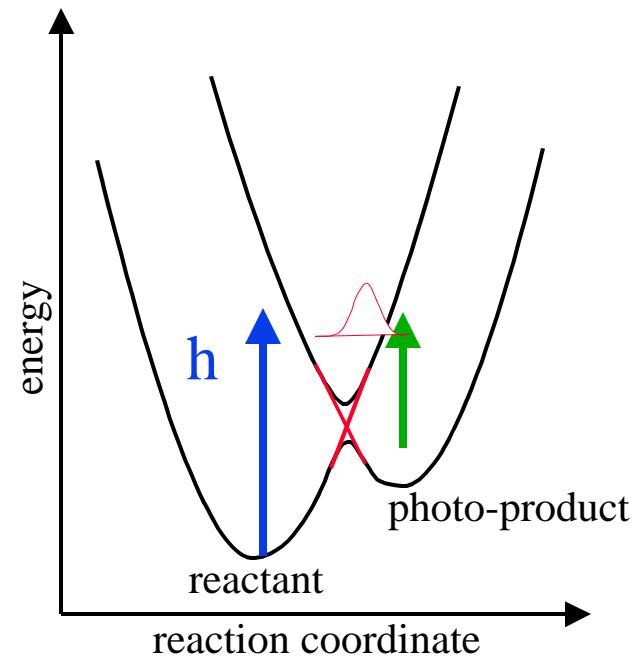
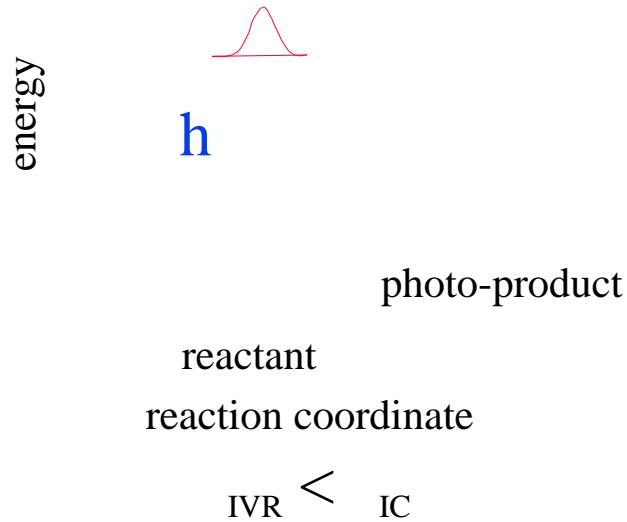
CdSe Nanocrystals: Solid-Solid Phase Transformation

A.P. Alivisatos et al. - U.C. Berkeley



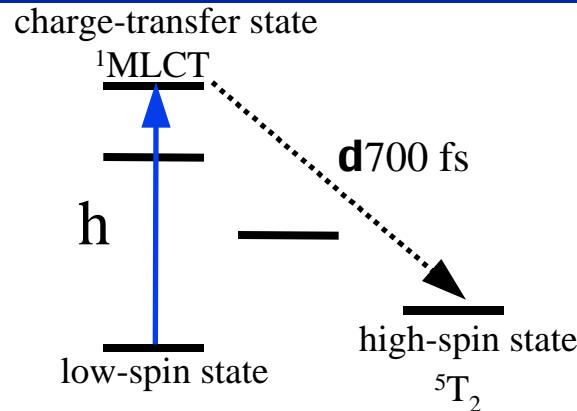
Ultrafast Chemical Reactions

Structural Dynamics of the Transition State



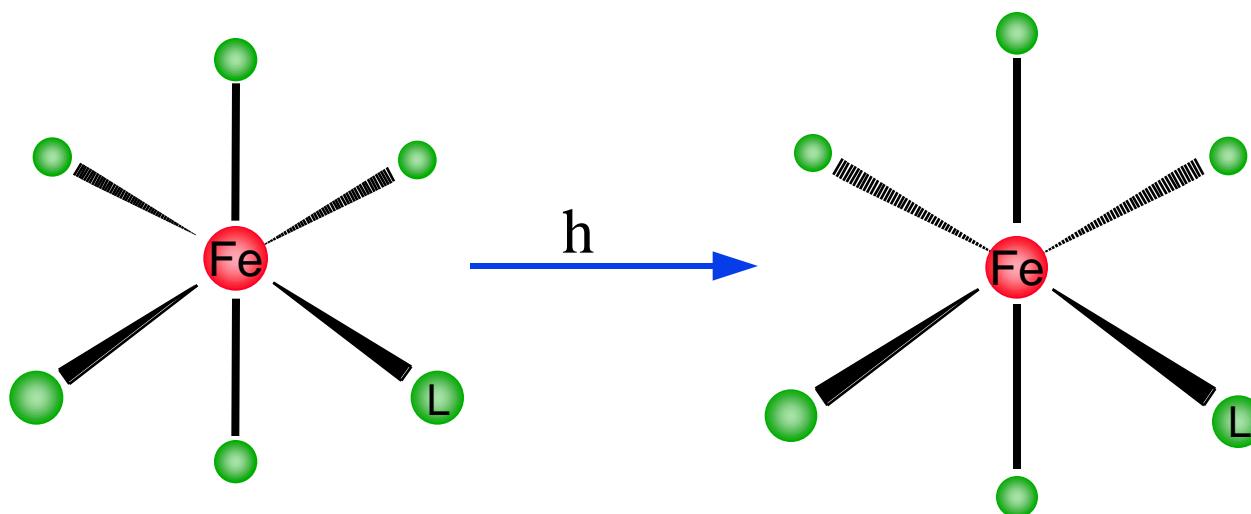
- intramolecular vibrational relaxation (IVR)
- internal conversion - IC

Fe^{II} Spin-Crossover Molecules



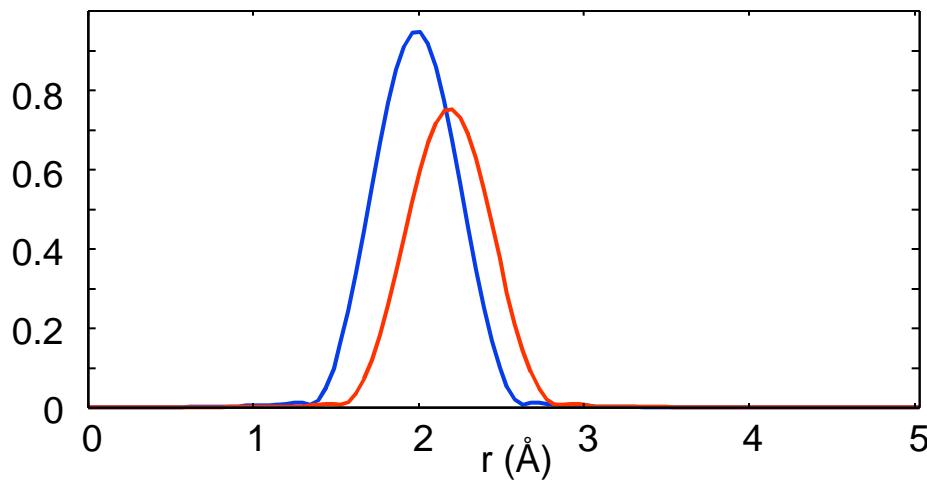
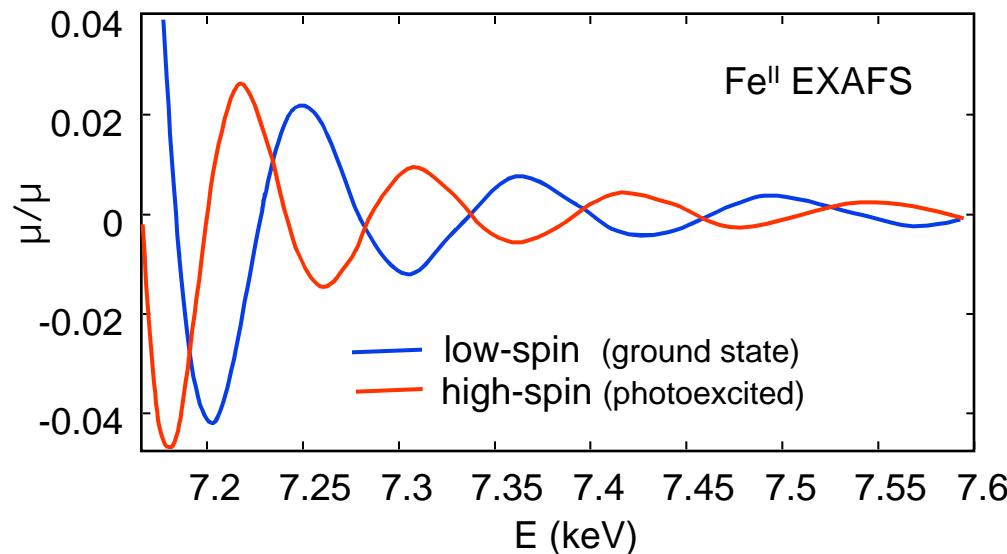
Scientific Interest

- role of structural dynamics in ultrafast spin crossover and electron transfer
- mechanistic role in biochemical processes (cytochrome P450)
- magnetic and optical storage material



- ~10-15% increase in metal-ligand bond distances
- structural dynamics concomitant with changes in optical and magnetic properties

Fe^{II} Spin-Crossover Molecules - EXAFS





Structural Dynamics of Ultrafast Biological Processes

Role of protein environment in chemical reaction?

Rhodopsin - photoreceptor for vision

- cis-trans isomerization complete in 200 fs
- vibrationally coherent

Heme Protein Dynamics

- structural changes associated with ligand binding and dissociation?
- vibrationally coherent photodissociation
(ultrafast optical spectroscopy)

Previous Time Resolved X-ray Diffraction and NEXAFS Studies

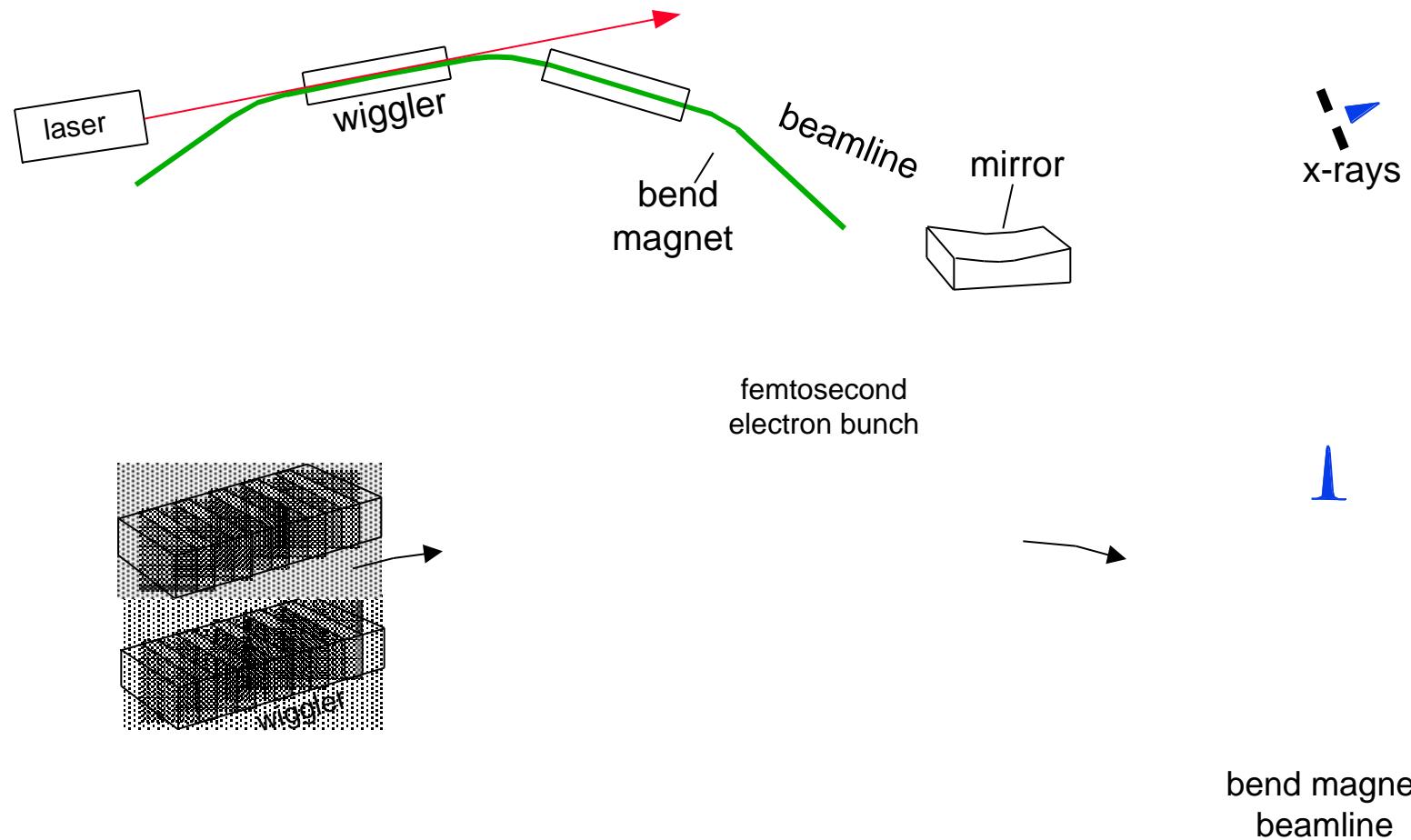
- | | | |
|---|------|-------------|
| • Bacteriorhodopsin photocycle | msec | DESY |
| • CO-myoglobin recombination | nsec | ESRF, CHESS |
| • Xanthopsin - photoactive yellow protein | nsec | ESRF |



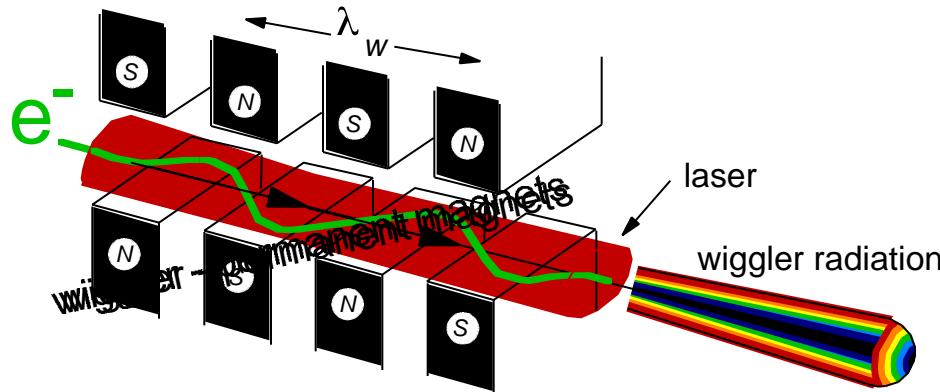
X-rays for Ultrafast Structural Dynamics

Characteristics for Ideal Source

- (1) temporal resolution 100 fs
 - pulse duration
 - synchronization to laser trigger
- (2) high average flux $10^8\text{-}10^{13}$ photons/sec/0.1% BW
 - high average brightness <1 mrad source divergence
- (3) tunable 0.3 keV - 20 keV
- (4) rep. rate: 100 Hz - 10 kHz



Energy Modulation in the Wiggler



$$\lambda_{radiated} = \frac{\lambda_w}{2\gamma^2} (1 + K^2 / 2) = \lambda_{laser}$$

resonance condition

amplitude of energy modulation

$$E = 2\sqrt{A_L A_R} \omega_L / \omega_R \cos\phi$$

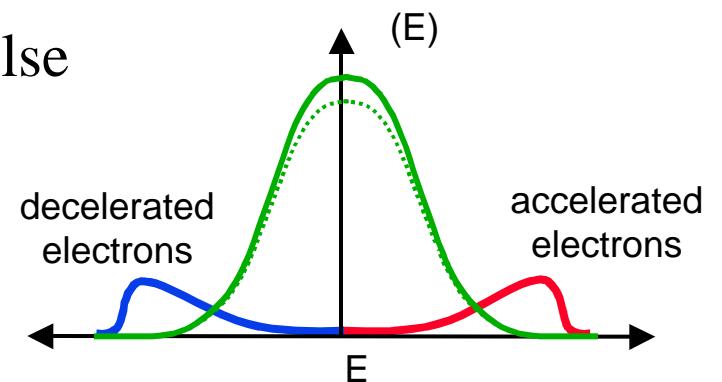
$$-\omega_L = 1.55 \text{ eV}$$

$\omega_L = 19$ period wiggler 25 fs laser pulse

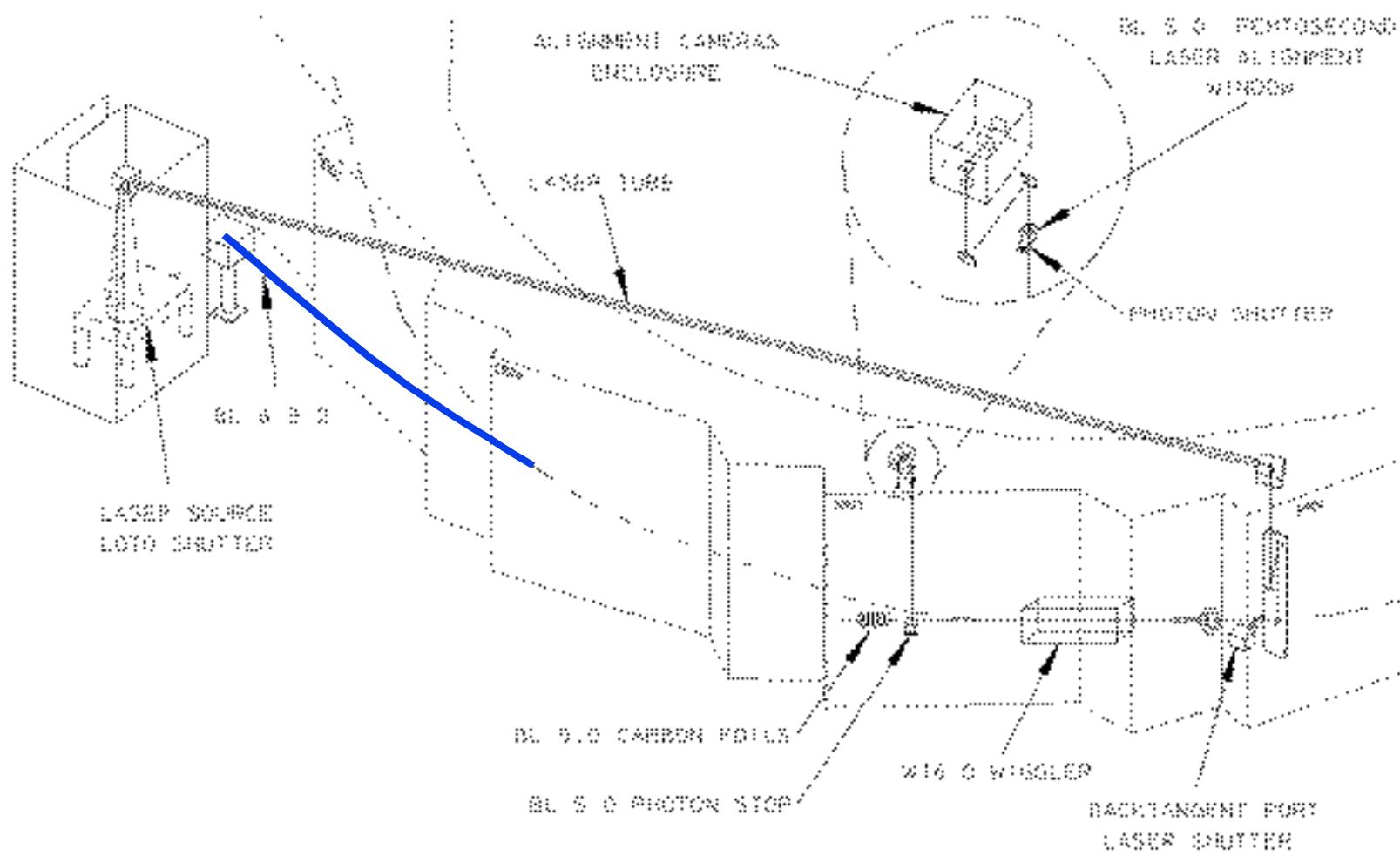
$$A_L = 100 \mu\text{J}$$

$E = 9 \text{ MeV}$

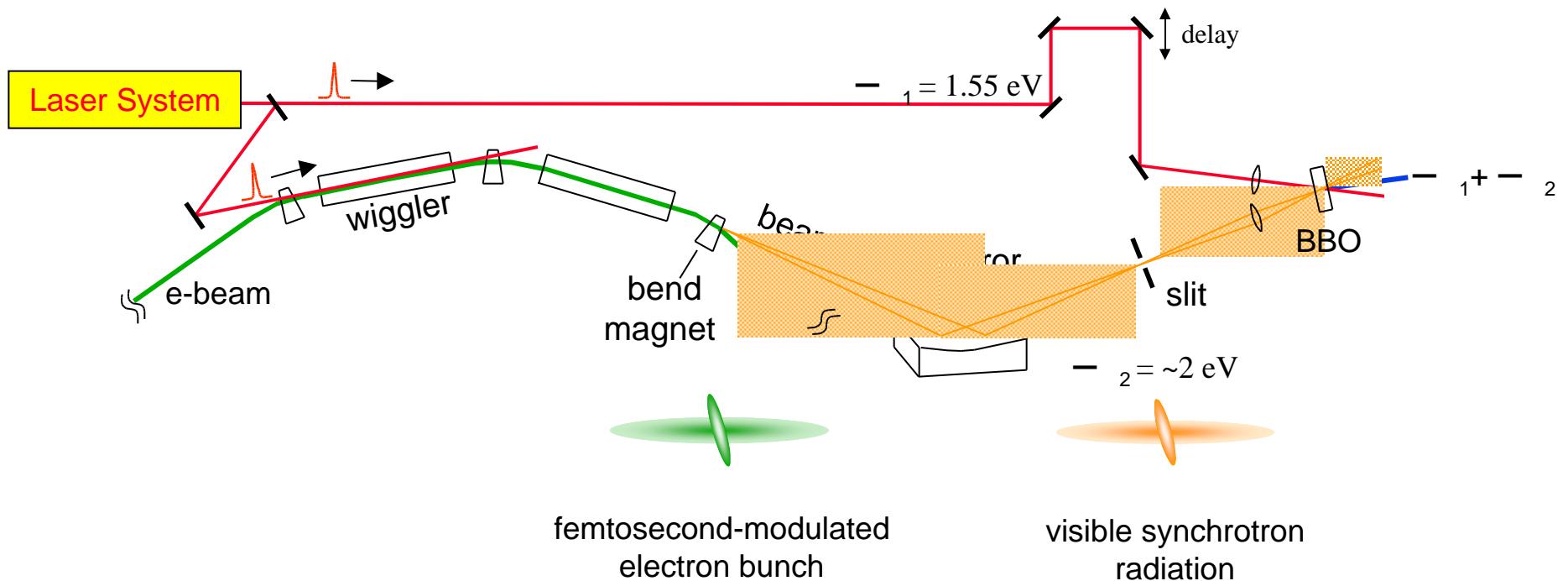
ALS beam energy spread $\sim 1.2 \text{ MeV}$ $E_0 = 1.5 \text{ GeV}$

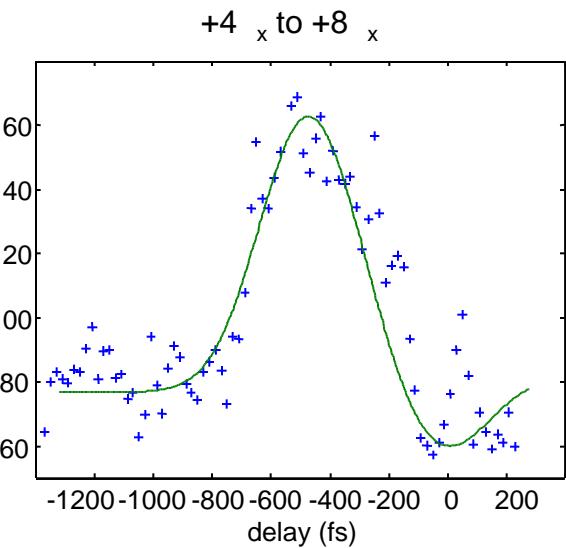
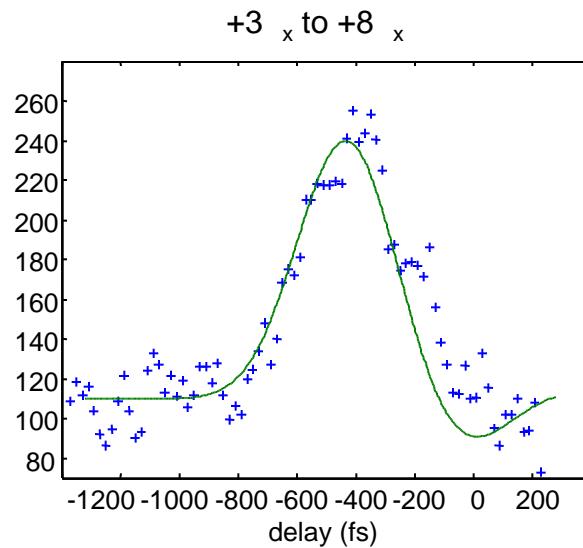
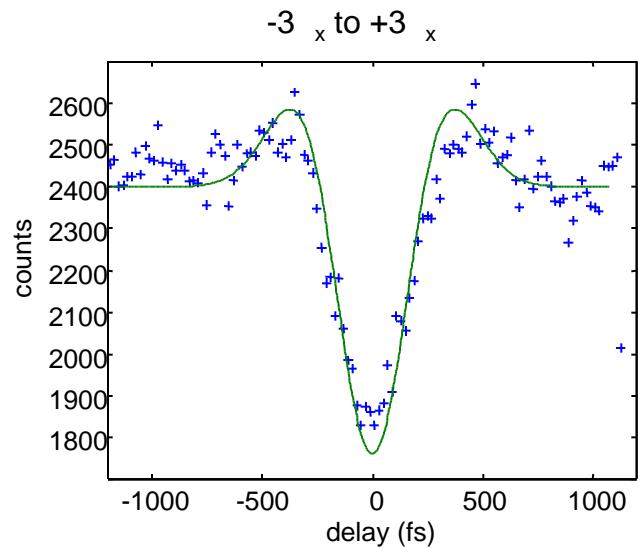


Synchrotron Beam Slicing - Layout

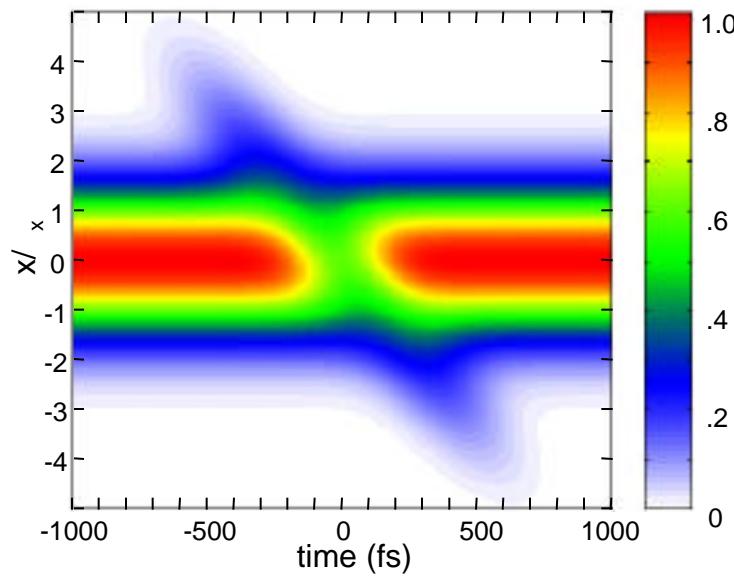


Measurement of Femtosecond Synchrotron Pulses via Frequency Upconversion





Calculated
Electron Density
Distribution



Schoenlein et al., *Science*, (in press).



Scientific Applications for Femtosecond X-ray Pulses

Time-resolved Measurements of Structural Dynamics in Condensed Matter

fundamental time scale for atomic motion - vibrational period ~100 fs

Solid-State Physics

- ultrafast phase transitions (solid/liquid and solid solid)

Chemistry

- structural dynamics of transition state - kinetic pathway of reaction

Biology

- structural dynamics - biological function and efficiency

ALS beamlines for ultrafast x-ray spectroscopy

- NOW*
- BEND: 10^8 ph/s/mm²/mrad²/0.1% BW, ~100 fs, 0.3-12 keV
- PROPOSED*
- UNDULATOR: 10^{11} - 10^{12} ph/s/mm²/mrad²/0.1% BW, ~200 fs, 0.5-10 keV